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Surface Design and Engineering Toward Wear-Resistant, Self-Lubricant Diamond Films and Coatings

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March 1999

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Chapter 10
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10.1 Introduction

High tribological reliability is of crucial importance in operating the many interacting surfaces that are in relative motion in mechanical systems [10.1]. The goals of tribological research and development are to reduce the adhesion, friction, and wear of mechanical components; to prevent their failure; and to provide long, reliable component life through the judicious selection of materials, coatings, surface modifications and treatments, operating parameters, and lubricants.

A notable amount of research effort has been put into fundamental studies of the tribological behavior of coatings. In recent years the increasing potential for the use of diamond films and diamondlike films as tribological coatings in mechanical systems has focused attention on these coating materials [10.2]. Tribological studies have been conducted with diamond and related coatings to understand better how the physical and chemical properties of these coatings will affect their behavior when in contact with themselves, ceramics, polymers, and metals [10.3–10.5].

Three surface design, surface engineering, and tribology studies have shown that the friction and wear of CVD diamond are significantly reduced in ultrahigh vacuum. This paper discusses the results of those studies: first, the friction mechanisms of clean diamond surfaces; second, the solid lubrication mechanism and the surface design of diamond surfaces; and finally, the actual tribological properties of the modified diamond surfaces and the selected materials couple. How surface modification and the selected materials couple (particularly the diamond–cubic boron nitride couple) improved the tribological functionality of coatings, giving low coefficient of friction and good wear resistance, is explained.

10.2 Friction Mechanism of Diamond Surface

10.2.1 General Friction Mechanism

The classical Bowden and Tabor model for sliding friction [10.6, 10.7], in its simple form, assumes that the friction force arises from two contributing sources. First, an adhesion force is developed at the real area of contact between the surfaces (the asperity junction). Second, a deformation force is needed to plow or cut the asperities of the harder surface through the softer. The resultant friction force is the sum of the two contributing sources: friction due to adhesion and friction due to deformation and/or fracture [10.6]. The adhesion arises from the attractive forces between the surfaces in contact. This model serves as a starting point for understanding how thin surface films can reduce friction and provide lubrication [10.8–10.10]. It should be realized, however, that one of the contributing sources acts to affect the other on many occasions. In other words, the two sources cannot be treated as strictly independent.

When a smooth diamond flat is brought into contact with a smooth spherical surface of diamond, ceramic, metal, or polymer, the plowing or cutting contribution in friction can be neglected. The friction due to adhesion is then described by the following equation [10.6]:

$$\mu = s\,A/W \qquad (10.1)$$

In this equation, μ is the coefficient of friction, s is the shear strength of the real area of contact, A is the real area of contact between the surfaces, and W is the load. Also, in such a basic contact condition, if we consider the total surface energy in the real area of contact, the coefficient of friction can be expressed as a function of γA

$$\mu = f(\gamma A) \qquad (10.2)$$

Here γA is the total surface energy in the real area of contact [10.11, 10.12]. To reduce friction and to provide lubrication, therefore, the shear strength s, the real area of contact A, and the surface energy γ must be minimized.

10.2.2 Specific Friction Mechanism

Because diamond has tetrahedral, covalent bonds between each carbon atom and its four nearest neighbors, the free surface may expose dangling bonds. Such a free surface has high surface energy γ, which is associated with dangling bond formation. When an atomically clean diamond surface contacts an atomically clean surface of counterpart material, the dangling bonds can form strong linkages with bonds on the counterpart surface. Many researchers [e.g., 10.2, 10.3, 10.7, 10.13] have found that atomically clean diamond has high adhesion and friction. For example, if the surfaces of natural diamond and metal are cleaned by argon ion bombardment, the coefficient of friction is higher than 0.4 in an ultra-high-vacuum environment. The coefficient of friction increases with an increase in the total surface energy of the metal in the real area of contact γA. With the argon-sputter-cleaned diamond surface there are probably dangling bonds of carbon ready to link up directly with metal atoms on the argon-sputter-cleaned metal surface. Thus, cleaning the diamond surface provided surface defects, such as dangling bonds, and accordingly high surface energy and enhanced adhesion and shear strength at the interface. The extremely great hardness and high elastic modulus of diamond provided a small real area of contact A. Because A was small but s and γ were large, the coefficient of friction for the argon-sputter-cleaned diamond surface was high in ultrahigh vacuum (Fig. 10.1).

The situation illustrated in Fig. 10.1 applies to sliding contacts of the CVD diamond surface with itself or other materials in ultrahigh vacuum [10.2, 10.6, 10.7, 10.9–10.15]. Without sputter cleaning or heating to high temperature in a vacuum, a contaminant surface film is adsorbed on the CVD diamond surface. The contaminant surface film can be removed when it repeatedly slides over the same track of counterpart material in vacuum. Then, a fresh, clean diamond surface contacts a clean surface of counterpart material, and a strong bond forms between the two materials. As a result the coefficient of friction for the diamond film becomes considerably high. As shown in Fig. 10.2, when a contaminant surface film was removed by repeatedly sliding a diamond pin over the same track of a diamond-coated disk in vacuum, the coefficient of friction increased from the initial value μ_I

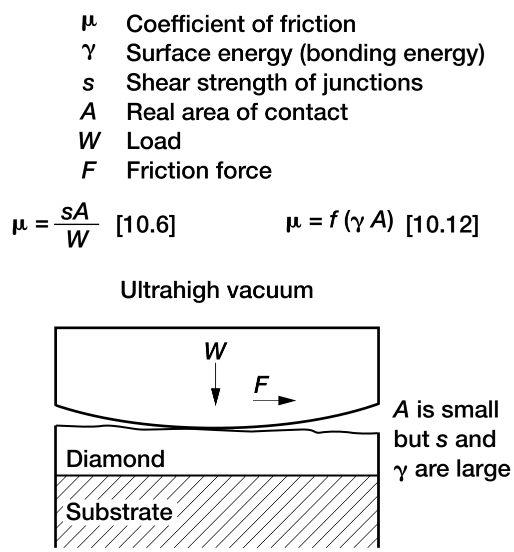

Figure 10.1.—Friction mechanism of clean diamond surface in ultrahigh vacuum.

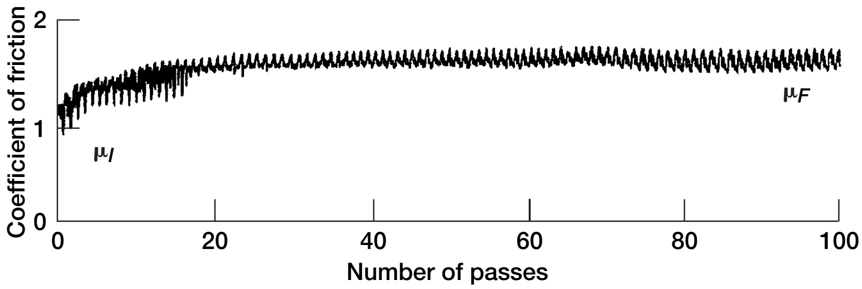

Figure 10.2.—Typical friction trace for bulk diamond pin in contact with diamond film deposited on alpha silicon carbide surface in vacuum (μ_I = initial coefficient of friction; μ_F = equilibrium coefficient of friction.)

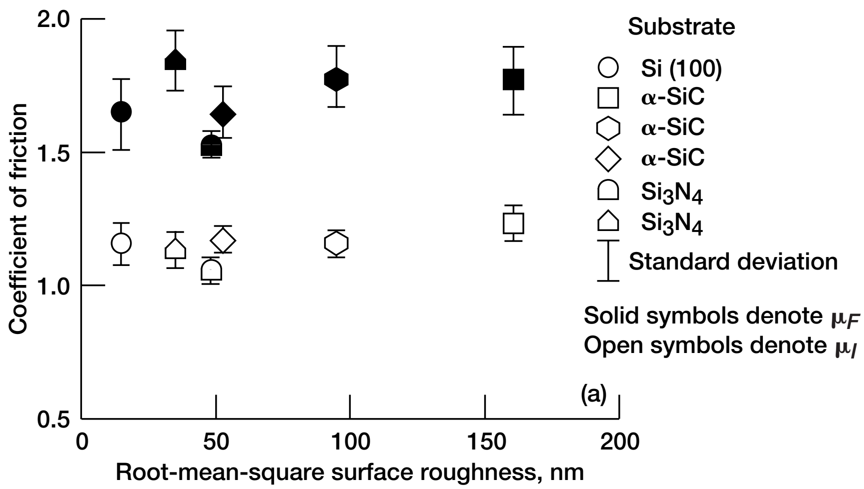

Figure 10.3.—Initial (μ_I) and equilibrium (μ_F) coefficients of friction and wear rates of diamond films in contact with natural diamond pin as a function of initial surface roughness of diamond film in ultrahigh vacuum. (a) Coefficient of friction. (b) Wear rate.

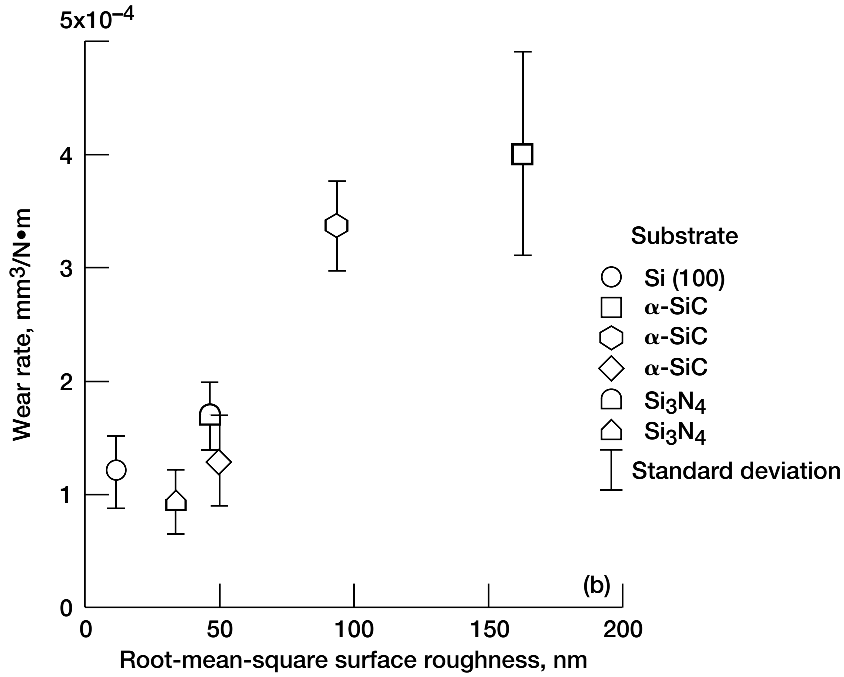

Figure 10.3.—Concluded. (b) Wear rate.

to the equilibrium value μ_F with an increasing number of passes. Figure 10.3(a) presents the initial and equilibrium coefficients of friction for a diamond pin sliding on various CVD diamond films in vacuum [10.13]. In all cases the equilibrium coefficients of friction (1.5 to 1.8) were greater than the initial coefficients of friction (1.1 to 1.3) regardless of the initial surface roughness of the diamond films. As shown in Fig. 10.3(b) the wear rate of the CVD diamond films in vacuum did depend on the initial surface roughness of the films, generally increasing with an increase in the initial surface roughness.

10.3 Solid Lubrication Mechanism and Design of Diamond Surface

According to the discussion and understanding described in the previous section, reducing the coefficient of friction requires minimizing the shear strength of the interface, the surface energy, the real area of contact, and the plowing or cutting contribution. Reducing wear generally requires minimizing these factors while maximizing the hardness, strength, and toughness of interacting materials. Toward this end, surface design and engineering can be applied to reduce the coefficient of friction and wear rate of CVD diamond.

μ Coefficient of friction
γ Surface energy (bonding energy)
s Shear strength of junctions
A Real area of contact
W Load
F Friction force

$\mu = \frac{sA}{W}$ [10.6]

Both s and A are small

$\mu = f(\gamma A)$ [10.12]

Both γ and A are small

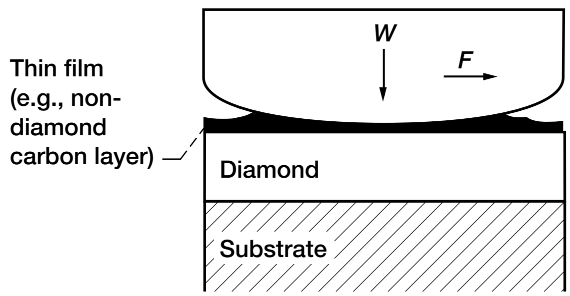

Figure 10.4.—Lubrication mechanisms.

Figure 10.4 illustrates how the minimization of the aforementioned factors can be achieved. In other words it shows how the presence of a thin film, such as nondiamond carbon on diamond, reduces the coefficient of friction. In the model presented, the thin film covers the diamond. The thin film can be any material, such as soft metal, polymer, ceramic, or a modified surface layer of the diamond, that has low shear strength or low surface energy. The underlying diamond reduces both the real area of contact and the plowing contribution of the counterpart material; a thin film or a thin surface layer reduces the shear strength and surface energy in the real area of contact. The low coefficient of friction can be attributed to the combination of the low shear strength and the low surface energy of the thin film or the thin surface layer and the small real area of contact resulting from the high elastic modulus and hardness of the underlying diamond film.

The coefficient of friction for clean interacting surfaces in ultrahigh vacuum strongly depends on the materials coupled. Figure 10.5 presents examples of the coefficients of friction for clean metal-metal couples, clean metal-nonmetal couples, and clean nonmetal-nonmetal couples measured in ultrahigh vacuum. The judicious selection of counterpart materials can reduce the coefficient of friction for diamond in ultrahigh vacuum.

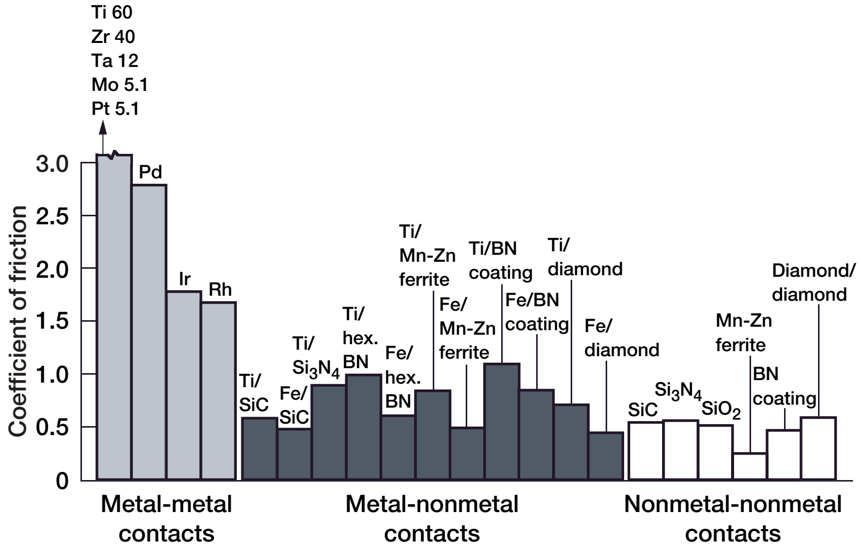

Figure 10.5.—Coefficient of friction for clean solid in sliding contact with itself or other material in ultrahigh vacuum.

10.4 Surface-Modified Diamond

10.4.1 Thin DLC Film on CVD Diamond

Figure 10.6 presents the steady-state (equilibrium) coefficients of friction and wear rates at room temperature in an ultrahigh vacuum (10^{-7} Pa). For a direct comparison the coefficients of friction and the wear rates were plotted from 10^{-2} to 10^{1} and from 10^{-8} to 10^{-3} $mm^3/N \cdot m$, respectively. An effective wear-resistant, self-lubricating material must generally have a coefficient of friction less than 0.1 and a wear rate on the order of 10^{-6} $mm^3/N \cdot m$.

As shown in Fig. 10.6(a) both the as-deposited, fine-grain CVD diamond film and the polished, coarse-grain CVD diamond film had high coefficients of friction (>0.4) and high wear rates (on the order of 10^{-4} $mm^3/N \cdot m$), which are not acceptable for solid lubrication applications [10.13–10.15].

As shown in Fig. 10.6(b) the thin film of DLC deposited on the as-deposited, fine-grain diamond by the direct impact of an ion beam resulted in low coefficients of friction (<0.1) and low wear rates (on the order of 10^{-6} $mm^3/N \cdot m$) [10.14–10.16]. The presence of a thin (<1 μm thick), amorphous, nondiamond carbon (hydrogenated carbon) film on CVD diamond greatly decreased the coefficient of friction

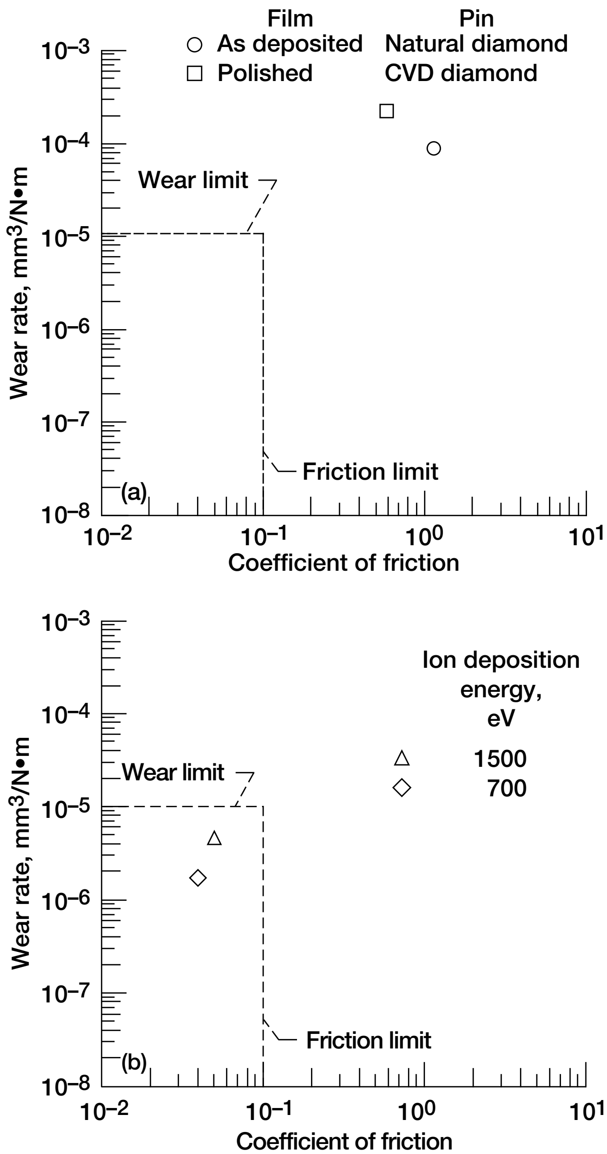

Figure 10.6.—Comparison of coefficient of friction and wear rate. (a) As-deposited diamond and polished diamond. (b) DLC films deposited on fine-grain diamond at 1500 and 700 eV. (c) Carbon-ion-implanted diamond and nitrogen-ion-implanted diamond.

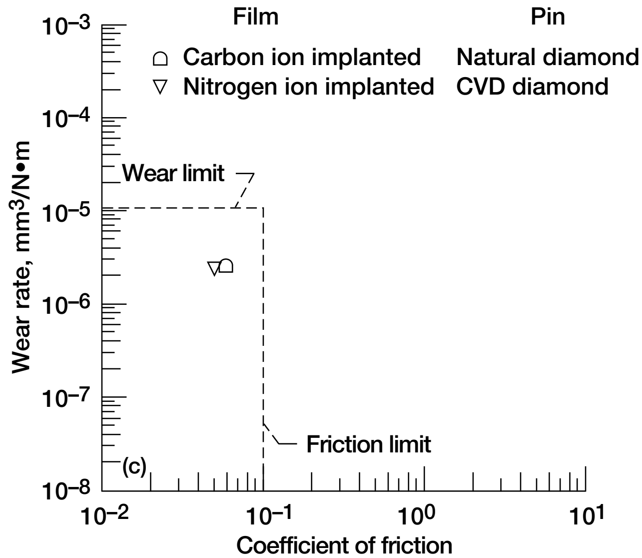

Figure 10.6.—Concluded.

and the wear rate. DLC on CVD diamond can be an effective wear-resistant, lubricating coating in ultrahigh vacuum.

Note that in dry nitrogen and in humid air (not shown) the coefficient of friction was less than 0.1 and the wear rate was on the order of 10^{-6} $mm^3/N{\cdot}m$ or less [10.16].

10.4.2 Thin Ion-Implanted Layer of CVD Diamond

The effect of carbon and nitrogen ion implantation on diamond's friction and wear properties was significant (Fig. 10.6(c)). Both carbon-ion-implanted diamond and nitrogen-ion-implanted diamond had low coefficients of friction (<0.1) and low wear rates (on the order of 10^{-6} $mm^3/N{\cdot}m$), making them acceptable for solid lubrication applications [10.15, 10.16]. Bombarding diamond films with carbon ions at 60 keV or with nitrogen ions at 35 keV produced a thin, superficial layer of amorphous, nondiamond carbon (<1 μm thick). This surface layer greatly reduced the coefficient of friction and the wear rate in ultrahigh vacuum to values that are acceptable for self-lubricating, wear-resistant applications of CVD diamond films.

Note that in dry nitrogen and in humid air (not shown) the coefficient of friction was less than 0.05 and the wear rate was on the order of 10^{-6} $mm^3/N{\cdot}m$ [10.15, 10.16].

10.5 Selected Materials Couple

Boron nitride is competing with diamond and silicon carbide in most applications, including friction-reducing coatings. Like for diamond a wide variety of synthesis methods are being used, and boron nitride can be grown in many phases. The cubic phase is the most desirable phase for applications [10.17]. Because cubic boron nitride (c-BN), which is chemically and thermally inert, is second only to diamond in hardness, many researchers believe that c-BN films offer great opportunities for wear parts, cutting tool inserts, rotary tools, and dies. The c-BN films are especially valuable for protective coatings on surfaces that come into contact with iron-based materials, where diamond cannot be used because of its high chemical wear due to its aggressive reaction with iron. Therefore, an investigation was conducted to examine the friction of c-BN in contact with diamond in ultrahigh vacuum. Reference experiments were also conducted in dry nitrogen and in humid air. The c-BN films (approx. 0.5 μm thick) were synthesized by magnetically enhanced plasma ion plating and formed on silicon {100} wafer substrates [10.18].

Figure 10.7 shows the low average coefficients of friction in ultrahigh vacuum for as-deposited c-BN films in sliding contact with CVD diamond pins as a function of the number of passes. This materials combination provided an effective self-lubricating, wear-resistant couple in ultrahigh vacuum at low numbers of passes. However, at approximately 1400 passes the sliding action caused the c-BN film to break down, whereupon the coefficient of friction rapidly increased (Fig. 10.7). The wear rate of this particular c-BN film sliding against a CVD diamond pin was on the order of 10^{-6} mm^3/N·m, but the wear rate of the CVD diamond pin was much lower.

Note that in dry nitrogen and in humid air (not shown) the coefficient of friction remained constant for a long period without breakdown even at 100 000 passes

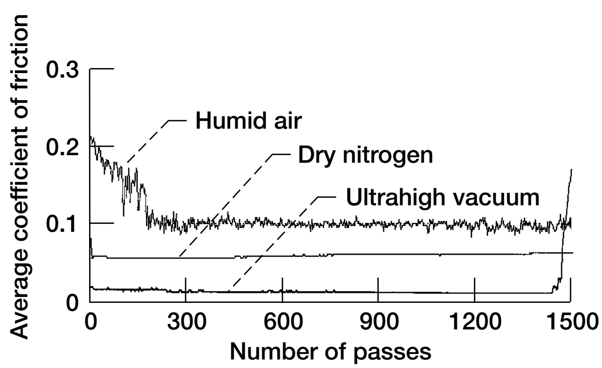

Figure 10.7.—Coefficients of friction for c-BN films in sliding contact with CVD diamond pins in humid air, dry nitrogen, and ultra-high-vacuum environments.

[10.16]. The endurance life of c-BN films was greater in dry nitrogen and in humid air than in ultrahigh vacuum by a factor of 60 or higher.

10.6 Conclusions

Three studies on the surface design, surface engineering, and tribology of chemical-vapor-deposited (CVD) diamond have shown that its friction and wear are significantly reduced in ultrahigh vacuum. The main criteria for judging the performance of diamond films to be an effective wear-resistant, self-lubricating material were coefficient of friction and wear rate, which had to be less than 0.1 and on the order of 10^{-6} $mm^3/N{\cdot}m$, respectively. The following conclusions were drawn from the results of these studies:

1. The presence of a thin film (<1 μm thick) of amorphous, nondiamond carbon (hydrogenated carbon, also called diamondlike carbon or DLC) on CVD diamond greatly decreased the coefficient of friction and the wear rate. Therefore, a thin DLC film on CVD diamond can be an effective wear-resistant, lubricating coating in ultrahigh vacuum.
2. The presence of an amorphous, nondiamond carbon surface layer formed on the diamond by ion implantation significantly reduced the coefficient of friction and the wear rate in ultrahigh vacuum to values that are acceptable for effective self-lubricating, wear-resistant applications of CVD diamond films.
3. CVD diamond in contact with cubic boron nitride exhibited low coefficients of friction in ultrahigh vacuum. Therefore, this materials combination can provide an effective self-lubricating, wear-resistant couple in ultrahigh vacuum.

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13. ABSTRACT ***(Maximum 200 words)***
This chapter describes three studies on the surface design, surface engineering, and tribology of chemical-vapor-deposited (CVD) diamond films and coatings toward wear-resistant, self-lubricating diamond films and coatings. Friction mechanisms and solid lubrication mechanisms of CVD diamond are stated. Effects of an amorphous hydrogenated carbon on CVD diamond, an amorphous, nondiamond carbon surface layer formed on CVD diamond by carbon and nitrogen ion implantation, and a materials combination of cubic boron nitride and CVD diamond on the adhesion, friction, and wear behaviors of CVD diamond in ultrahigh vacuum are described. How surface modification and the selected materials couple improved the tribological functionality of coatings, giving low coefficient of friction and good wear resistance, is explained.

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